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SEMI-ANNUAL STATUS REPORT NO. 5 ON SPECTROSCOPIC STUDY
OF SOLAR AND PLANETARY ATMOSPHERES

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SEMI-ANNUAL STATUS REPORT NO. 5 THE NATIONAL AERONAUTICS
AND SPACE ADMINISTRATION

"SPECTROSCOPIC STUDY OF SOLAR AND PLANETARY ATMOSPHERES"

NAME AND ADDRESS OF INSTITUTION: GEORGETOWN UNIVERSITY
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Work Performed: This report is divided into four areas, the first area is the Simulation of the Martian Atmosphere, the second is the Fluorescence of NO_2 , the third is Summary and Correlation of Previous Observations, and the last includes other work which does not fall under the first three categories.

Mars was observed during all or part of 26 nights from February 4th through April 9th. The discussion of these observations appears in Report No. 4. We are continuing to observe the planets on every available night. This series of plates represents a nearly continuous set of observations which will take considerable time to analyze. They also represent a permanent record that will enable future investigators to study other problems in connection with planetary atmospheres.

The fluorescence of NO_2 was extensively studied as will be reported in area two.

A library search was made for all previously recorded Martian phenomena. All astronomical literature written in English, French, German, Russian, Spanish and Italian was surveyed. This large task could only be economically justified using low cost highly qualified high school and college students. We felt that we had a unique opportunity under our summer intern program in that we had students fluent in so many

foreign languages. The results of this study are presented in area three.

The Martian fly-by, Mariner IV, provided further comfort to us that we are probably on the correct track, and that some of our critics have been a bit over enthusiastic. We now are quite sure that water vapor does not exist in appreciable quantities on Mars, and that there is a high probability that we will be able to convincingly show the existence of significant quantities of nitrogen peroxide in the Martian atmosphere.

Area 1. Laboratory spectra - Simulated Martian Atmosphere.

A. Equipment Improvements

After many set-backs we now feel that our laboratory equipment is capable of obtaining highly significant absorption spectra of gases which are observable at pressures less than atmospheric. If we are to observe gases at greater than atmospheric pressures then we will have to design and fabricate additional equipment. The main problem in obtaining accurate pressures of nitrogen peroxide is that it is a polymer, and therefore the perfect gas law does not hold. If the perfect gas law held we would merely have to obtain an initial pressure and temperature, and all other pressures would be determinable merely by measuring the temperature.

A further problem which we have not completely solved is the fact that N_2O_3 is formed when nitrogen peroxide is subjected to ultraviolet sun-light. We can observe this change when passing the sun's light through our optical tube. As soon as the sun's light first passes through the optical tube our electrical conductivity gauge (similar to the Pirani type) takes approximately 15 minutes to stabilize. Once we have reached stabilization we have no present means of determining the partial pressures of NO_2 , N_2O_4 and N_2O_3 . If accurate determinations of partial pressures under ultraviolet conditions is desired in the future, some means of measuring the partial pressures will have to be developed.

This will more than likely consist of taking small samples of the gas and subjecting them to chemical analysis, which we are not equipped to do at present.

A study of the reflectance spectrum of solid N_2O_4 was performed using especially built cold fingers immersed in nitrogen peroxide. These cold fingers were built at no cost to the project, and the work was performed by a highly qualified high school student. Since we felt that there would be little or no concrete results in the visible range we did not charge the project for this work. It only enabled us to cross off one more possibility, and also enabled the student to perform an experiment which took top honors in the Virginia State Science Fair.

B. Results

It has become more and more obvious that NO_2 is a difficult molecule to observe. During the summer at Georgetown Observatory we mapped the whole photographic spectrum of NO_2 . Some of the results are shown in Figures 1, 2 and 3. On each plate we have either one or two comparison spectra from an iron arc. The iron spectrum appears in emission and is shown by the bright lines as shown on the positive reproduction. The comparison spectrum is used to accurately determine the wave lengths. In addition the continuous spectrum of the black body source is placed on the upper-most portion of each plate. This gives an indication of the plate's sensitivity to the black body source. Finally, three or four absorption spectra using the black body were photographed on each plate.

It was found in order to map all regions of the spectrum of NO_2 , that path length and exposure times were highly critical. By examining the figures it becomes immediately apparent that often only a few hundred angstroms could be mapped at a time. To the short wavelength side complete absorption occurs and to the long wavelength side no absorption appears. Therefore, it is unjustified to say that since a certain band of NO_2 does not appear in the Martian spectrum then NO_2 does not exist.

Mr. Brian T. O'Leary of the Berkeley Astronomical Department and Space Sciences Laboratory, University of California published an article in PASP volume 77, number 456, page 168, June 1965, entitled "A Revised Upper Limit of NO_2 in the Martian Atmosphere". Mr. O'Leary received his master's degree from Georgetown University in 1964. Mr. O'Leary apparently was not aware of the fact that one has to match the densities of exposure of the planet Mars and the lunar comparison spectrum at approximately H_α (6562 λ). The purpose of this is to have equal photographic densities in a region where little NO_2 absorption is expected.

Once the above procedure is followed the Martian spectrum is highly absorbed toward the blue, which is apparent from all photographic plates that we have taken. On page 172 of his article he presents tracings of the Moon and Mars under matched density conditions between 4460 to 4500 λ . He also shows laboratory tracings of NO_2 which incidently were taken directly from his Georgetown University thesis. He concludes that since he can not see the NO_2 band at 4480 λ that there is a low concentration of NO_2 . What he has completely neglected is the fact that the NO_2 might completely blanket this region and not show up even if it is there. This complete blanketing effect is apparent from our laboratory spectrum (figures 1, 2, and 3). All of the Georgetown Observatory plates are matched at H_α . We therefore have a very strong tool to measure the path length of NO_2 . We now can examine each Martian plate, look for the transition region where the Martian plate changes from no absorption to complete NO_2 absorption, identify the NO_2 features in the transition region if they are present, and since the wave length region of the apparent features is so critically a function of pathlength we have high hopes of using this tool to obtain quantitative path lengths.

At present we are scanning our Martian plates in order to locate the transition region. This work will be quite laborious, but we feel that we are coming quite close to the final determination of this problem. We also feel that this problem should be resolved as soon as

possible in order to better guide the designers of soft landing vehicles on the Martian surface. If indeed there is nitrogen peroxide in large quantities in the Martian atmosphere then the vehicle will have to be protected from this highly corrosive and lethal gas.

Area 2. Fluorescence of NO₂:

A. Background

The fluorescence spectrum of NO₂ has been studied by R. G. W. Norrish (J. Chem. Soc. p 1611, 1929) and by D. Neuberger and A. B. F. Duncan (J. Chem. Phys., 22, 1693, 1954). These investigators all used spectrographs of relatively low dispersion (e.g. 37 Å/mm at 4358 and 300 Å/mm at 7200 Å) and they did not give detailed descriptions of the spectrum. Norrish reported bands from about 5000 Å to 6650 Å with evidence of a very faint emission between 4500 Å and 4800 Å. The main emission was confined to two broad bands at 6250 Å to 6550 Å and 5600 Å to 6050 Å. Neuberger and Duncan describe the spectrum as extending from the exciting line (4358 Å or 5461 Å) to about 8000 Å (the long wavelength limit of observation).

The spectrum was observed at gas pressures of from 1 mm to 40 mm of Hg. W. P. Baxter (J. Am. Chem. Soc., 52, 3920, 1930) reported maximum intensity for total nitrogen peroxide pressures at 0.02 to 6 mm of Hg. The overall intensity of the spectrum was found to be stronger when 4358 Å excitation was used than when 5461 Å excitation was used.

It is apparent to us that a more exact description of the fluorescence spectrum of NO₂ is needed in order to investigate the possibility that fluorescence in NO₂ may be affecting the observed absorption spectrum of planetary atmospheres.

B. Equipment improvements

The illumination system for the focus scale and for the internal comparison scale for the Georgetown Observatory Littrow

Spectrograph was repaired and converted from battery power to a 6 volt a. c. system. The plate tilt (rotation about a vertical axis) indicator was found to be slipping and it was removed and repaired. Due to the slippage it was necessary to re-establish the correct plate tilt adjustment for each focus position by trial and error.

Focussing plates were taken by using the focus settings from the table of values provided with the instrument. All but one focus setting resulted in poorly focussed exposures. Therefore a series of focus plates was made to determine the correct focus setting for each position (each position corresponds to a different wavelength region). Good focus was obtained for each of the positions 2 through 9 (corresponding to the wavelength region from 2300 A to 6600 A).

Installation of a power supply for a d. c. arc light source was completed. A spark power supply is also available.

The chief requirements for fluorescence spectroscopy is an intense source of sharply monochromatic radiation of a wavelength corresponding to the energy difference between two energy levels of the molecule being studied (G. R. Harrison, R. C. Lord and J. R. Loofbousew, Practical Spectroscopy, Prentice Hall, p. 293, 1948). The correspondence need not be exact so long as the minimum energy required is available. In previous studies of NO_2 fluorescence filtered light from mercury arcs was used as a source of excitation.

The experimental arrangement generally used for fluorescence spectroscopy was first described by R. W. Wood (Physical Optics, Mac Millan, 1923). This requires a glass or quartz tube having a flat window on one end and a horn shape on the other end. The tube is illuminated from the sides and the fluorescence is viewed through the flat end window. The purpose of the horn shape at the opposite end is to minimize the amount of stray, reflected light which reaches the spectrograph. Due to the fact that we were time-limited, we had to use our present optical tube which has both ends flat.

Mercury arcs are the most commonly used light sources. The intensity of the illumination can be increased by using from 1 to 12 arcs in conjunction with mirrors or lens type collimators. In our work we used only one mercury arc as we were concerned with overheating the optical tube. If we are to continue this program we would probably want to cool the optical cell with a liquid filter solution.

The chief requirements of a spectrograph for fluorescence spectroscopy are: high speed ($f/10$ or better), moderate resolving power and fair dispersion. A compromise usually must be made between speed and dispersion. Wood noted that the Littrow mount is disadvantageous for this type of work because of the relatively large amount of stray reflected light. Blazed grating spectrographs are satisfactory as well as high speed prism instruments. Georgetown Observatory's Wadsworth mounted grating spectrographs give too high dispersion for this type of work, therefore we had to use our Littrow, however, we had no fogging of our plates which overcomes Wood's objection.

The optical tube was illuminated with a single 100 watt laboratory mercury arc lamp. In conjunction with the lamp a condensing lens was used. The filter used was one of the following: Corning Noviol shade A (3-73) which transmits above 4200 A, an interference filter with 16% maximum transmission, and a 10 A half width centered at 4360 A. The spectrograph used (Hilger E1) is a Littrow mounted quartz prism spectrograph with a speed of $f/20$.

C. Results

A faint streak of orangish light could be seen through the end window. A number of plates were exposed in the spectrograph. Mercury and iron arc spectra were taken on the same plate for comparison spectra. Even though the fluorescence could be seen visually, only on two plates was any fluorescence detected and this was very faint. However, this might have been fluorescence in the filter rather than fluorescence in

the NO_2 . Therefore, the results of the attempt to photograph the fluorescence spectrum of NO_2 have been almost entirely negative.

D. Future Work

Since there was no problem of fogging the plates, it seems that the Georgetown Observatory Littrow spectrograph is a satisfactory instrument. In addition, since fluorescence was observed visually, an increase in power input seems to be the answer. Therefore, we are planning to attempt the following lines of attack.

1. Borrow a more powerful mercury source for feasibility studies.
2. Put Hg 198 light directly through the tube of NO_2 , which will result in a Hg 198 spectrum with (possibly) NO_2 modifications (absorption) and fluorescence.
3. Borrow a ruby laser for feasibility studies.
4. Look for a laser near 4360 Å, however, this would be a very special unit.

Area 3. Summary and Correlations of Previous Observations:

A literature search for all previously recorded Martian clouds was conducted during the summer of 1965. All astronomical literature written in English, French, German, Russian, Spanish and Italian was surveyed.

Three forms of Martian clouds were catalogued, yellow, white and the planet-wide blue-obstructing layer often called "blue haze". Yellow clouds appear bright in yellow or red light, but are not detectable in blue light. White clouds appear bright visually, but are generally transparent to red light. Occasionally, clouds appear bright in blue light only, and are called "blue clouds". Both white and blue clouds have been determined to be crystalline by observations in polarized light (Physical Properties of the Planet Mars, Douglas Report SM-43634 p 65). Yellow clouds have been considered by many investigators to be dust. However, Dollfus has shown that while terrestrial dust clouds polarize light positively,

the yellow clouds polarize negatively. This would tend to indicate that the yellow clouds are not dust, but they could be clouds of nitrogen dioxide which is a redish brown gas, which polymerizes to nitrogen tetroxide, a colorless gas and a white solid.

Pertinent data are available during the last 80 years which cover 5 cycles of Mars being near perihelion at opposition. From these data several significant correlations were established.

1. Yellow clouds were shown to occur at the periods of maximum warmth during the Martian year, that is, following the Martian solstices and at perihelion. This would be an expected characteristic if nitrogen peroxide were present.

2. White clouds tend to occur during cold periods and tend to peak at aphelion. This would be an expected characteristic if frozen nitrogen tetroxide were present.

3. Both types of clouds appear to be influenced by the amount of polar cap material as determined by the variation in their size. The greatest number of yellow clouds occur when there is a minimum amount of material trapped in the polar caps. This occurs following the winter solstice of Mars at about 60° heliocentric longitude. White clouds exhibit a pronounced peak following both equinoxes, when the polar caps begin to melt and/or sublime.

4. Perhaps the most significant correlation found was that between yellow clouds and blue clearing. Yellow clouds do not occur during blue clearing, which indicates that one is inhibiting the other. If yellow clouds are nitrogen dioxide gas, then during periods of yellow clouds and haze, the Martian atmosphere would be filled with a blue-absorbing layer. During periods of yellow cloud minimum there should be little nitrogen dioxide in the atmosphere, and consequently if the scattering layers were also absent, blue clearing would result.

A summary of this literature search will be published in an appropriate periodical, and the complete data will be published as a Georgetown Observatory Monograph.

Area 4. Other Work:

As previously reported in semi-annual report No. 4 we have submitted our results which tend to negate the presence of water vapor on Mars to the Astrophysical Journal. These results have been examined by a referee, our modifications have been made, and our paper has been resubmitted for publication.

The paper as reported in semi-annual report No. 4 for which Dr. Carl Kiess acted as a referee has been published. This paper is by Mr. Brian T. O'Leary, entitled "A Revised Upper Limit of NO_2 in the Martian Atmosphere," and appears in PASP volume 77, number 456, page 168. Much of his data was obtained at Georgetown Observatory and credit is given to NaG-362. As mentioned previously we do not agree with Mr. O'Leary's conclusions, however, we have no control over how he interprets our data as he is no longer in our employment.

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page eleven

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Financial Report

C. f. University Nonprofit Institutional Management Report
(forwarded by University Treasurer's Office).

Figure 1

SPECTRAL MAP OF NITROGEN DIOXIDE

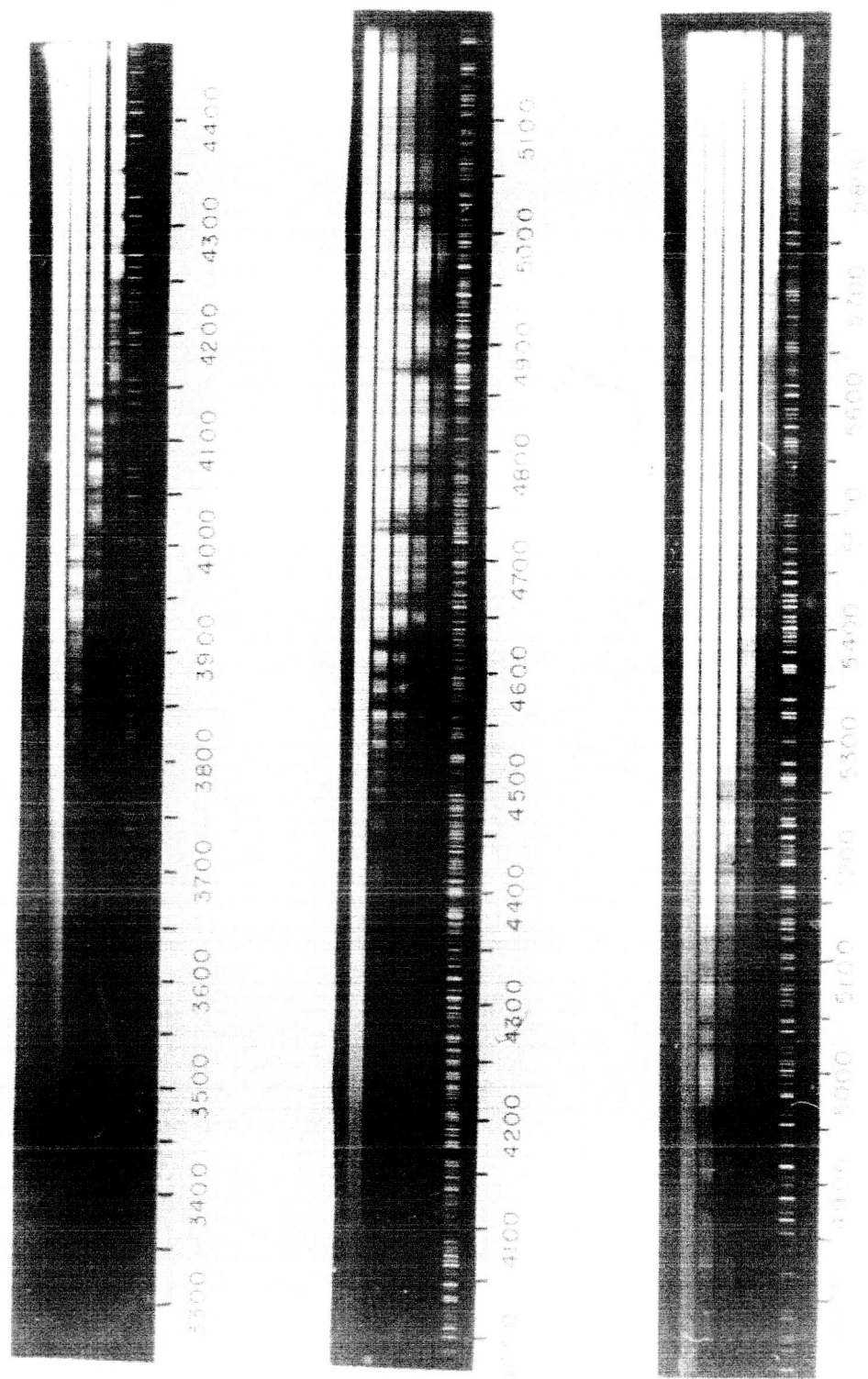


Figure 2

SPECTRAL MAP OF NITROGEN DIOXIDE

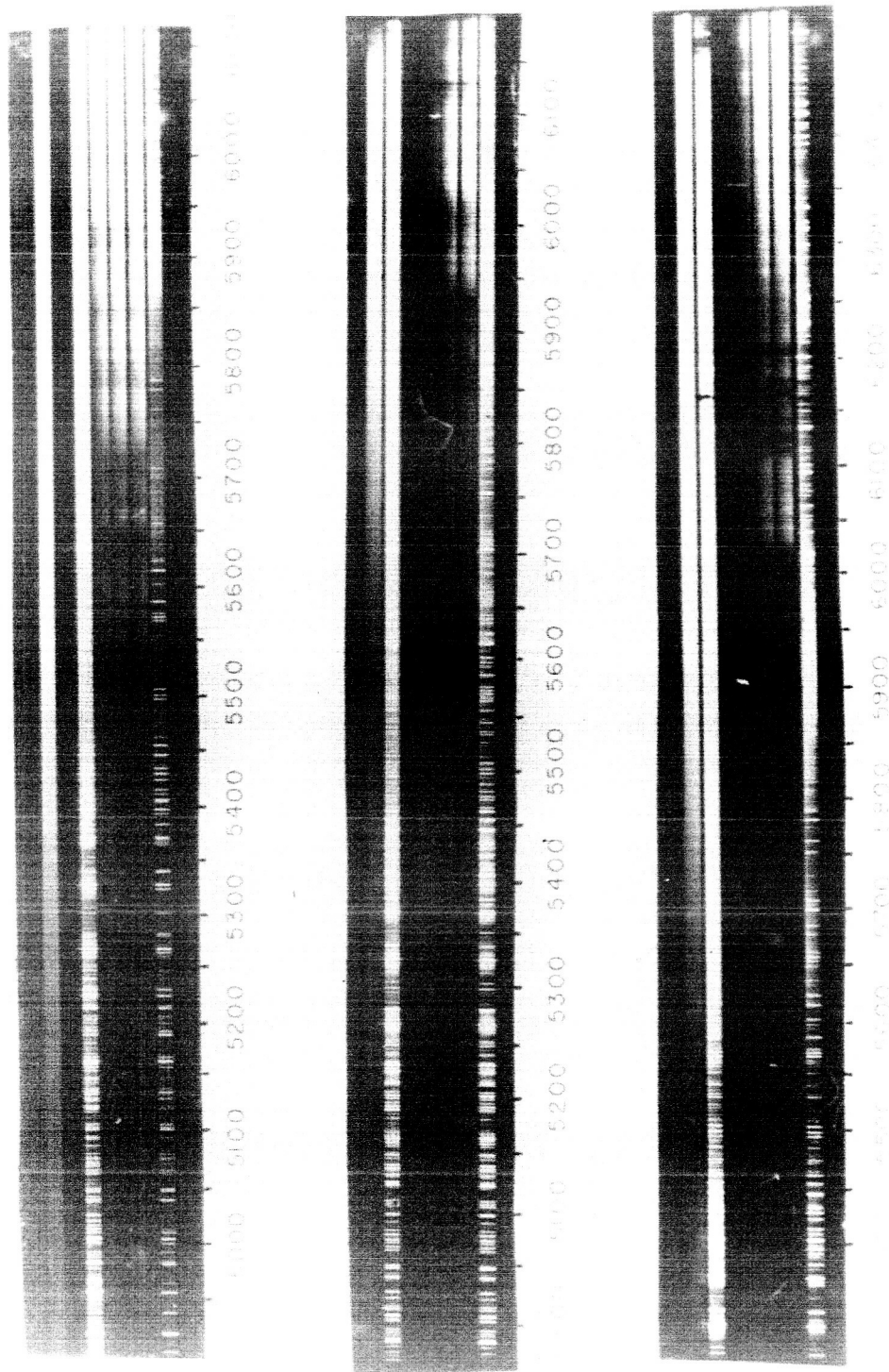


Figure 3

SPECTRAL MAP OF NITROGEN DIOXIDE

